

# CHEMICAL INTERACTIONS BETWEEN LINEAR AND CYCLIC ALKANES DURING PYROLYTIC DEGRADATION OF JET FUELS

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## ABSTRACT

Potential jet fuels derived from hydrogenation of liquids from coal and petroleum fractions, are rich in both cycloalkanes and long-chain alkanes. Their thermal interactions have been studied using decahydronaphthalene and n-tetradecane as model compounds. Chemical interactions were indicated in the pyrolytic regime by the decrease in gaseous products with increasing addition of decahydronaphthalene to the n-alkane. The improved thermal stability of the n-tetradecane was mainly attributed to the ability of the cycloalkane to capture free radicals from the cracking of the n-alkane.

## INTRODUCTION

There is an increasing demand of improved thermal stability of jet fuels for high Mach flights, as illustrated by the JP-900 requirement of the Air Force (1). However, the present aviation jet fuels do not meet these criteria, due to their high content of alkanes in the range  $C_7$ - $C_{17}$ , which readily lead to thermal degradation (2). The JP-900 goal has been approached by jet fuels derived from coal liquids (3). Coal derived jet fuels differ substantially from those generally obtained from petroleum in their high content of cyclo-alkanes and a relatively lower concentration of linear alkanes. This chemical distinction is one of the main reasons why coal derived fuels show greater thermal stability in the pyrolytic regime than those of petroleum origin (4). Cyclo-alkanes alone show a great chemical stability in the pyrolytic regime (5). However, due to economical concerns, other potential routes to obtain cyclo-alkane rich fuels are considered, including hydrogenation of aromatic petroleum fractions or by blending of coal and petroleum derived fuels (4). These fuels will still present a relatively high content of long-chain linear alkanes. Earlier tests in batch reactors have shown reduced solid depositions in petroleum fuels at 450°C with addition of decahydronaphthalene (6). This suggests a synergistic effect between the linear and the cyclic alkanes at elevated temperature. Accordingly, this study addresses the chemical interactions between cyclo-alkanes and n-alkanes typical for coal and petroleum derived fuels, where decahydronaphthalene was used as a cyclic model compound, while n-tetradecane represented the linear alkanes.

## EXPERIMENTAL

The compounds used were n-tetradecane (TD, Aldrich 99%) and decahydronaphthalene (DHN, Aldrich 98%, a mixture of 46 mole% cis- and 54 mole% trans-decahydronaphthalene). Stressing of TD alone or in 5 or 30 mole% mixtures with DHN were performed for 2 hours in a fluidized sandbath at 425, 450 and 475°C. A detailed description of the experimental setup and analytical determination of the product distribution using GC and GC/MS, has been reported elsewhere (4).

## RESULTS AND DISCUSSION

Figure 1 compares the gas, liquid and solid yields on a weight basis for pure n-tetradecane (TD) and the mixtures of 5 and 30 mole% decahydronaphthalene (DHN) in TD stressed for 2 hours under an initial pressure of 100 psi  $N_2$  at the

temperatures 425°C (a) and 475°C (b). The development of solids at both temperatures shows the same trend, where the pure TD has a higher value than those observed for both the mixtures. This is especially the case at 475°C, where the pure TD deposited nearly 5 wt% solids compared with around 3 wt% for the mixtures. The liquid residue is in addition lower for the pure TD than for the mixtures (Figure 1). Even at temperatures as low as 425°C, the liquid yield increased from around 82 wt% for TD alone to 97 wt% with only 5 mole% DHN added. Assuming that virtually all the DHN stays in the liquid product (based on evidence discussed later), this corresponds to a relative decrease in the gaseous product from the TD of  $(18-3.2)/18 = 80\%$ . Similar data was obtained at 450°C. This clearly indicates that DHN prevents gas and solid formation when compared with TD alone. Figure 2 shows that this thermal enhancement is closely related to the reduced cracking of the TD, where the GC traces of the liquid product distribution for TD alone (top) and its mixture with 30 mole% DHN (bottom) stressed at 425°C, are plotted. A great reduction in the cracking products is obtained, where their distribution is shifted towards longer alkanes and 1-alkenes.

Tables 1 to 3 list the total reaction products based on the initial amount at 425, 450 and 475°C for the pure TD and its 5 and 30 mole% DHN mixtures, respectively. With increasing DHN addition, there is a decrease in the amount of linear or branched alkanes at all temperatures, which is also the case for alkenes. The cyclo-alkanes, on the other hand, become more important at higher temperatures, but there is no clear relation to the DHN concentration. Some small amount of alkylated DHN, such as n-butyl-decalin, are also included in these values. In further studies at shorter stressing time (30 minutes), where secondary reactions are expected to be low, a significant amount of ethyl- to dodecyl- substituted decahydronaphthalenes were detected in the liquid products. However, at the relatively long stressing times used here, these intermediates have generally been converted into hydroaromatics (tetralin, alkylated tetralin and indanes) or completely dehydrogenated into naphthalenes (7). However, the increased addition of DHN markedly reduces the development of benzenes, where at 475°C, TD alone produced 23 mole%, while the mixture with 30 mole% DHN only gave 16 mole% benzenes.

The fraction of TD remaining over the initial amount is compared in Figure 3 for the pure TD and its mixtures with 5 and 30 mole% DHN at 425, 450 and 475°C. At 425°C, the increasing content of DHN significantly prevents the thermal decomposition of the TD, where with no DHN added only 40 mole% TD remains compared to nearly 80 mole% for the 30 mole% DHN mixture. Even though this trend is decreasing when the temperature becomes more elevated, there is still a significant rise in the TD content obtained at 450°C with only 5 mole% DHN. After 2 hours stressing at 475°C, the TD has almost vanished and the stabilization effect of the DHN is most likely affecting shorter linear alkanes based on the enhancement in the liquid yield and suppression of solid deposition (Figure 1). Figure 4 compares the remaining DHN over its initial concentration for the 5 and 30 mole% mixtures at 425, 450 and 475°C. Around 90-100 mole% remains up to 450°C followed by a sudden drop at 475°C to around 30-45 mole%. The values are higher for the 5 mole% DHN mixture, as an estimated value of 0.5 % in the calculations gives  $0.5/5=10\%$  error in this values (see error bar). The small reduction in DHN concentration at 425 and 450°C is related to stabilization of free radicals via alkylation of the DHN, as discussed earlier. This suggests that DHN at high contents is a benign prohibitor of thermal decomposition of TD up to 450°, due to its own thermal stability.

At increasing temperatures, the benzenes and naphthalenes concentrations are increasing for TD stressed alone and its 5 and 30 mole% DHN mixtures (Tables 1 to 3). The mixtures with DHN are expected to contain a certain amount of naphthalenes due to the dehydrogenation process it experiences during the chemical interaction with the free radical products from the cracking of the TD. Therefore, the total content of naphthalenes must be considered on the basis of the consumed content of DHN. Figure 5 compares the content of naphthalene, where the consumed content of DHN is subtracted, at 450 and 475°C for the pure

TD and its 5 and 30 mole% DHN mixtures. Although resulting in higher overall concentrations of naphthalenes (Tables 1 to 3), Figure 5 illustrates that the naphthalene developed is decreasingly resulting from thermal decomposition of TD as the addition of DHN is increased. This again supports the previous findings that the DHN in mixture with TD prevents thermal decomposition of the n-alkane by suppressing its decomposition into small alkanes and the production of naphthalenes or more condensed aromatic products.

## CONCLUSIONS

Tetradecane (TD) has been stressed alone and in mixtures with 5 and 30 mole% decahydronaphthalene (DHN) at 425, 450 and 475°C. A significant decrease in the solid deposition and increase in liquid yields were observed at all temperatures with the addition of DHN. Further, the content of TD remaining was greatly enhanced at temperatures up to 450°C, but was not significant at 475°C due to the thermal decomposition of DHN itself.

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Table 1: Distribution of the total reaction products based on the initial amount at 425, 450 and 475°C for the pure TD.

Products / mole%	425°C	450°C	475°C
Alkanes C <sub>14</sub>	22.1	31.6	11.7
Alkanes C <sub>14</sub> <sup>+</sup>	1.8	6.5	<0.1
Cyclo-alkanes	5.1	7.6	7.5
Alkenes	11.7	3.4	1.0
Hydro-aromatics	<0.1	1.8	2.7
Benzenes	<0.1	11.5	23.0
Naphthalene	<0.1	0.9	6.7

Table 2: Distribution of the total reaction products based on the initial amount at 425, 450 and 475°C for the 5 mole% DHN in TD mixture.

Products / mole%	425°C	450°C	475°C
Alkanes C <sub>14</sub>	20.3	27.4	13.1
Alkanes C <sub>14</sub> <sup>+</sup>	7.2	0.6	0.1
Cyclo-alkanes	7.8	8.1	9.5
Alkenes	8.9	1.9	1.3
Hydro-aromatics	<0.1	1.0	3.0
Benzenes	0.1	7.6	21.2
Naphthalene	<0.1	1.8	4.8

Table 3: Distribution of the total reaction products based on the initial amount at 425, 450 and 475°C for the 30 mole% DHN in TD mixture.

Products / mole%	425°C	450°C	475°C
Alkanes C <sub>14</sub> <sup>-</sup>	4.8	15.2	3.6
Alkanes C <sub>14</sub> <sup>+</sup>	1.0	0.5	<0.1
Cyclo-alkanes	3.2	8.0	6.5
Alkenes	2.4	2.2	1.7
Hydro-aromatics	<0.1	3.4	4.4
Benzenes	0.1	7.1	16.0
Naphthalene	<0.1	3.1	14.2

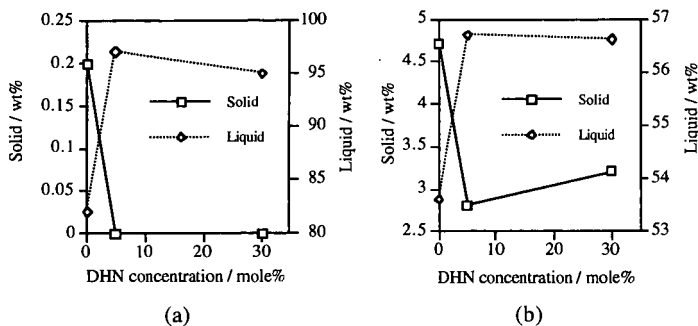


Figure 1. Comparison of liquid and solid yields for pure TD and its mixtures with 5 and 30 mole% DHN stressed for 2 hours under an initial pressure of 100 psi N<sub>2</sub> at the temperatures: (a) 425°C and (b) 475°C.

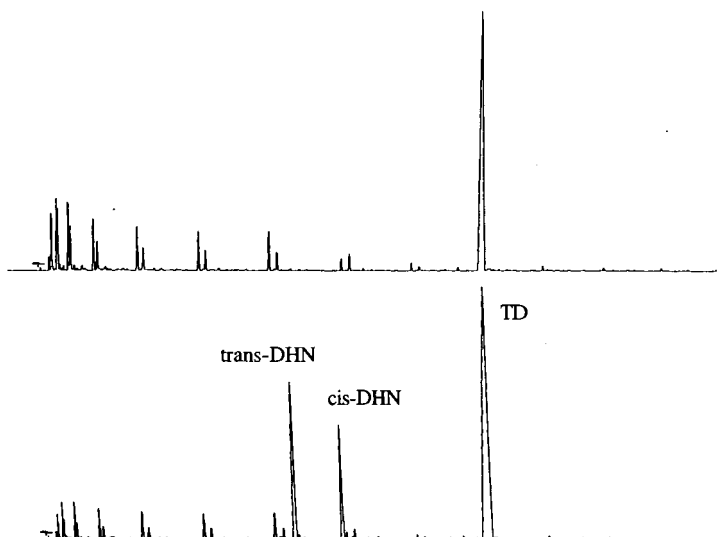


Figure 2. The GC traces of the liquid product distribution for TD alone (top) and its mixture with 30 mole% DHN (bottom) stressed at 425°C.

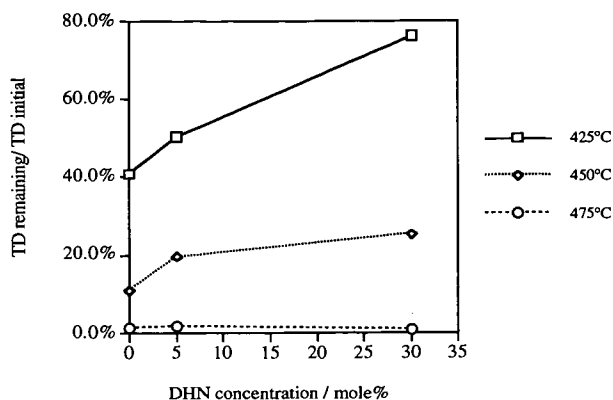


Figure 3. The fraction of TD remaining over its initial concentration for TD alone and its mixtures with 5 and 30 mole% DHN at 425, 450 and 475°C.

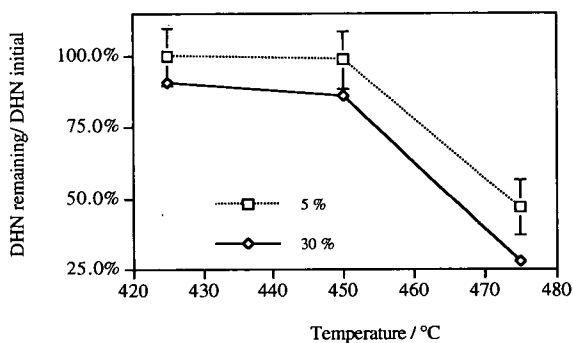


Figure 4. Comparison of the remaining DHN over its initial concentration for the 5 and 30 mole% mixtures with TD at 425, 450 and 475°C.

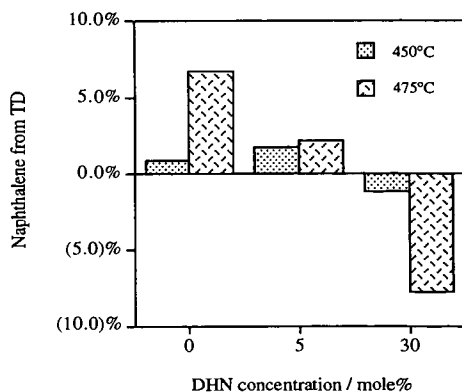


Figure 5. Comparison of the content of naphthalenes where the consumed content of DHN is subtracted at 450 and 475°C for the pure TD and the 5 and 30 mole% DHN in TD mixtures.